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Photographs: The XDC Analyser from Brookhaven Instruments

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Particle size distribution is key to new high-performance UV absorbers

Once favoured only by lifeguards and mountaineers, sunscreens based on zinc oxide are now one of the coolest forms of skincare. New transparent zinc oxide formulations rely on accurate measurement of particle size distribution to combine cosmetic appeal with powerful ultraviolet-stopping ability.

Zinc oxide has a long and honourable history as an ingredient in skin-care products. It has been used as a treatment for skin irritations for more than 300 years and, more recently, as an effective shield against solar radiation.

Until just a few years ago, sunscreen preparations based on zinc oxide were far from glamorous. The thick white creams were fine for beach lifeguards and other sturdy outdoor types, but had less appeal for fashion-conscious consumers wanting to look good around the pool. Titanium dioxide, the only other inorganic contender in the sunscreen stakes, is even more opaque than zinc oxide. As a result, organic ultraviolet (UV) absorbers such as benzophenone (oxybenzone), octyl methoxycinnamate and 4-aminobenzoic acid (PABA) dominated the market for sunscreen compounds because of their translucent properties.

Now zinc oxide is making a comeback. Technical advances in manufacture and formulation allow the use of zinc oxide particles less than 200nm across — fine enough to appear almost completely transparent, yet effective across the full UV spectrum, from the short-wavelength UVB (290-320nm) to the longest Type I UVA (340nm-400nm).

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Supporters of zinc oxide claim that no single organic UV absorber can match this spectral range. In addition, they say, zinc oxide gives high sun protection factors (SPFs), is economical to use, is completely stable on exposure to sunlight and causes no skin problems. Many organic sunscreens, by contrast, have been implicated in irritation and allergies.

Checking particle size using X-rays

sunSmart Inc., based in Wainscott, New York, is the world's largest supplier of the new "transparent" zinc oxide for sunscreens. The company's Z-COTE product – now supplied by BASF Corporation - is a patented microfine zinc oxide with a particle size of less than 0.2µm and a tight particle size distribution (PSD).

In fact, the PSD is so important that sunSmart Inc. ran quality control (QC) tests for PSD on every fourth batch of Z-COTE it manufactured. It is critically important to measure the PSD of the zinc oxide precisely and with high resolution.

Central to the QC process is an XDC particle size analyser manufactured by Brookhaven Instruments of Holtsville, New York. The XDC is an X-ray disc centrifuge: it uses X-ray absorption to measure the mass of particles as they settle out of the test sample, either under the influence of gravity or when centrifuged. The particle size is calculated from the settling time using Stokes law, which predicts the speed at which small particles fall through a liquid.

Stokes settling is a well-accepted and well-understood method. There are no optical corrections or mathematical deconvolution algorithms to apply. The instrument can measure particle size distribution from tens of microns down to deep submicron, and measurements take place in real time — it is not just a 'black box'. In addition, the instrument is straightforward to use, and clean-up between samples or runs is simple.

sunSmart has used the Brookhaven instrument for several years. Before buying the XDC, the company also looked at competitive laser-diffraction instruments, but decided that the XDC was the only device with the necessary resolution over the range of particle sizes of interest. It was recommended by colleagues at Du Pont, experts in the field of particle size analysis, who provided a copy of a report compiled on the comparison of various techniques for particle size analysis.

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Measuring the finished product

As a mainstay of the QC laboratory, the XDC analyser works hard for its living. The instrument is in operation up to 12 hours a day, often seven days a week. It measures the actual PSD of zinc oxide in a unique way because X-rays are absorbed by materials like metal oxides, ceramics and refractories, but they pass through organic materials like carbon blacks, oils and polymers. Consequently, although the simplest form of measurement is on a sample of zinc oxide powder dispersed in water, the XDC can also measure particle size distribution in a real finished product, such as a sunscreen lotion.

Measuring the finished products is very important because no matter how good the PSD is when the zinc oxide is manufactured, what really matters is the PSD in the final formulation. If the particles are aggregated then the product will not appear transparent — it may even feel gritty. The SPF per percentage of zinc oxide in the formulation will also be lower, so a higher concentration of zinc oxide will be needed to achieve the desired SPF.

The XDC is incredibly useful in allowing the comparison of zinc oxide with other active ingredients, such as titanium oxide, and with competitive products.

Sunscreen performance: expectations rise

Now that zinc oxide is available in a cosmetically-attractive transparent form, its stability and gentleness on the skin should be enough to give it wide acceptance as the active ingredient in sunscreen formulations. In 1998, the American Academy of Dermatology said that zinc oxide is a physical block that is not absorbed, so it does not cause any allergic reactions. This is especially important to look for if you have sensitive skin or are using sunscreens on a daily basis.

But there are other issues, too. Increasingly, consumers expect sunscreens to protect them not just from sunburn, but also from the other effects of exposure to the sun: skin cancer and ageing of the skin. As a result, they are buying many other cosmetic products, which contain sunscreens, for daily use.

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In the past, doctors blamed short-wavelength UVB and medium-wavelength UVA II radiation (320nm-340nm) for skin cancer and photoageing. Within the last few years, however, evidence has grown to show that the long-wavelength UVA I may also be involved. The mechanisms of attack vary; while UVB, for instance, can directly damage DNA in the skin cells, UVA I is more likely to show its effects by catalysing the formation of reactive oxygen species, which then go on to damage skin cells.

Most organic sunscreens block only UVB or UVA II. Zinc oxide is unusual in that it absorbs uniformly all the way from UVC (below 290nm) right into the UVA I range, with a sharp cut-off at around 380nm. Particle sizes in the range 0.1–0.2μm give the best combination of UV attenuation and aesthetics.

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Three steps to a perfect dispersion

When is a particle not a particle? When it's an aggregate or an agglomerate. Zinc oxide in a typical sunscreen product exists not as individual crystals — the primary particles — but particle aggregates: groups of two or more primary particles that have bonded irreversibly together during the manufacturing process. Primary particles never make up more than a tiny fraction of the zinc oxide present, whereas aggregates predominate in a well-prepared dispersion.

If the dispersion has not been properly made, groups of aggregates may stick together to form agglomerates. Because they act like individual large particles, agglomerates are less transparent than aggregates. If they are large enough they may feel gritty, and they absorb UV less effectively than the same mass of smaller particles. Agglomerates are therefore to be avoided.

In the past, achieving uniform and stable dispersions of fine powders in liquids used to be seen as a black art. But it is actually quite simple as long as you understand the physical and chemical properties of the materials involved.

Dispersion consists of three separate steps — wetting, de-agglomeration and stabilisation.

Good wetting is critical to achieving a stable dispersion later. If the solid resists wetting, this step may require a surfactant to reduce the surface tension of the liquid. If the solid wets easily, surfactants should be avoided.

The next step, de-agglomeration, generally needs a chemical aid to break up agglomerates. De-agglomerating agents, which are different from surfactants, work by increasing the repulsive electrostatic forces between the particles making up the agglomerates.

The final step, stabilisation, refers to the use of either electrostatic or steric forces to stop the dispersion from settling out. Steric forces (the use of absorbed layers) are preferred for liquid-liquid emulsions. For inorganic particles such as zinc oxide, control of electrostatic forces (zeta potential) is the commonest method. Coating particles of zinc and titanium oxides with silica, for instance, can allow them to co-exist in a stable suspension at pH values that would cause the uncoated particles to precipitate.

Problems in making stable dispersions have led to a rise in the popularity of pre-dispersed pigments and other active ingredients. However, such pre-dispersions don't guarantee the stability of the final formula and may introduce unnecessary additives. A better approach is to start from a dry powder and follow the three-step dispersion procedure, using only those additives that are actually needed.

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